

LABORATORY STUDIES ON HIGH TEMPERATURE-SHORT TIME
STERILIZED EVAPORATED MILK. I. EASILY CONSTRUCTED
ECCENTRIC FALLING BALL TYPE BOMB MICROVIS-
COMETERS SUITABLE FOR CONTAINING BIOLOGICAL
MATERIALS DURING STERILIZATION AND STORAGE

SUMMARY

A simple eccentric falling ball type bomb microviscometer is described. This instrument, which lends itself to easy construction in large numbers, is suitable for containing, sterilizing, and storing of milk, milk concentrates, and other biological liquids. Samples as small as 0.01 ml. may be processed and stored. Viscosity measurements may be made before and after sterilization and during storage. The operational characteristics of these microviscometers have been considered in the light of the empirical and semiempirical relationships which apply to falling ball viscometers of the eccentric type. These relationships have been shown to extend to the very small diameter tubes and spheres employed in the construction of the bomb microviscometers. The effect of the angle of inclination on the instrument constant has been determined and this effect furnishes a basis for the rejection of malfunctioning viscometers.

Food products and biological materials, in general, which are to be preserved for any length of time, require sterilization. When this is brought about by the employment of high temperatures, deleterious physicochemical changes in the material may occur. An important criterion of quality modification is change in the body or consistency of the product. A suitable related measurement is that of the rate of shear attending the application of a definite shearing stress.

The rate of shear may be proportional to the shearing stress. Fluids for which this relation holds are classified as Newtonian and truly viscous. All other fluids are non-Newtonian and are by definition only apparently viscous. For these, the viscosity index is not independent of the rate of shear but varies with it and/or with the history of the sample.

The need for adequate laboratory techniques in gelation studies on concentrated sterile milk led to the development of a microviscometric technique particularly suitable to such studies. Inasmuch as the microviscometric technique is one which may have a broad biological application in all fields where the determination of the viscosity of micro samples is desired, the construction and operation of the viscometer are discussed, along with certain relationships necessary for the intelligent use of the instrument.

APPARATUS AND METHODS

In high temperature-short time sterilization, the bringing-up time must be quite rapid in comparison with the short holding time. Since it was desired to sterilize samples in the measuring device, this criterion limited the material

for construction of the microviscometers to thin-walled capillary tubing. The microviscometer was, therefore, made to consist of a thin-walled capillary tube and a small glass bead operating on the principles of the well known Höppler viscometer (2); this permitted measurements on samples as small as 0.01 ml. to be made. The microviscometer also served as a bomb in which samples could be sterilized at temperatures above their boiling point. This permitted viscosity measurements to be made on the samples before and after sterilization and during storage, with a minimum disturbance of the sample.

The microviscometer was constructed from tubing, the bores at the ends of which approximated 0.45 mm. Measurement of bore diameter was made by the use of a tapered beading needle and a microscope equipped with an ocular micrometer. For relatively precise work, tubes were selected approximately 5 cm. in length, the bores at the ends of which were the same to within 0.003 mm.

Glass beads were obtained from the Minnesota Mining and Manufacturing Company¹ in sizes ranging from 28-470 μ in diameter. Preference in this investigation was given to beads in the range 250-375 μ . Rolling of the beads during transfer was prevented by impregnating the surfaces on which the beads were lodged with glycerol. Bead diameters were determined microscopically and transfers made by means of a sharp-pointed tweezer. Distorted beads were largely eliminated by a procedure in which beads were permitted to roll on the smooth base of a rectangular optical cell inclined at an angle of approximately one degree. Only those beads were selected which traversed the cell from one edge to the opposite one in the shortest time.

Tubes were cleaned in a conventional manner by aspirating through them in succession hot detergent solution, water, and acetone. Capillary action was used to partially fill each tube with sample. A leakproof closure of the clean end was made by sealing around a glass bead positioned in the end of the tube. The trapped air cell in the tube was removed by centrifuging at approximately 500 \times gravity. Through the remaining open end a bead of predetermined diameter was forced into the sample, using a pipette probe. The wall of the viscometer located above the liquid level was cleaned by inserting a drawn glass capillary tube to a point above the liquid level, immersing the tube in water, and aspirating. The clean open end was then sealed and expanded slightly to give an air-tight seal. The position of the fluid thread in the tube was reversed by centrifuging and, simultaneously, trapped air was eliminated.

To measure viscosity, the tube banded to a thermometer was oriented with its axis parallel to the thermometer thread. The thermometer inserted into a 500-ml. cylindrical water-bath was aligned in a vertical position by means of a stopper and a mark at the base of the cylinder. The water-bath was then strapped on to the slant side of truncated blocks of known side angle. At the time a measurement was made, the block in front of a titrator lamp was rotated 90° about a horizontal axis. The time required for the bead to move 2.25 cm., or multiples as fractions thereof from a point 0.7 cm. from the base

¹ It is not implied that the U. S. Department of Agriculture recommends the above company or its product to the possible exclusion of others in the same business.

of the tube, was noted. Densities needed for calculation purposes were determined pycnometrically, and the viscosity of glycerol solutions needed for standardization was measured with a Bingham viscometer (1).

The microviscometer was emptied of calibrating fluid without removing the bead, by first severing the end portions of the viscometer, constricting the open ends, and removing the glycerine by suction. The cleaned, dried capillary tube was then filled with sample in the manner already prescribed.

RESULTS AND DISCUSSION

Viscometer constant. The principles underlying the use of viscometers of the eccentric fall type are well known (5). The high precision instrument, the Höppler falling ball viscometer, is widely used. Governing its use is the empirical equation:

$$(1) \eta = kt (\rho_b - \rho_f) \text{ also written}$$

$$(2) \eta = \frac{C}{v} (\rho_b - \rho_f)$$

These equations also govern the use of the microviscometer. In the equations η is the viscosity, ρ_b and ρ_f are, respectively, the densities of the spherical bead and fluid, t is the transit time between two marks on the viscometer, 10 cm. apart in the Höppler instrument, v is the velocity of fall, and k or C are instrument constants. The determination of the instrument constant does not lend itself to treatment based on theoretical hydrodynamics. Dimensional analysis, however, provides a clear insight into the relationships involved (3, 5).

The viscometer constant may be shown to be proportional to the square of either the bead or tube diameter, and to a function of the ratio between the bead diameter and the tube diameter, thus:

$$(3) C = f\left(\frac{d}{D}\right) d^2 g (\rho_b - \rho_f) \cos \theta$$

The symbols d and D represent, respectively, the diameters of the bead and tube, $f\left(\frac{d}{D}\right)$ is a function of the dimensionless variable $\frac{d}{D}$, g is the gravitational constant, and θ is the inclination of the tube to the vertical. The function, $f\left(\frac{d}{D}\right)$ is independent of either d or D and, therefore, if evaluated under one set of conditions it should be valid under any other set.

Figure 1 shows two graphs, one referring to the Höppler instrument (5), the other to the microviscometer. The log of the instrument constant k is plotted against the log of the difference between the tube and bead or ball diameter. A linear relation holds for small values of $D-d$. The slope of the line is within experimental error the same, both for the microviscometer and the Höppler instrument. The microviscometer constant k in the region of small $D-d$ is equal to $0.006 D^{-1/2} g (D-d)^{2.5}$. The corresponding equation for the Höppler instrument in good agreement contains the constant 0.0057 in place of 0.006. The curves pass through a maximum located at approximately the same value of the

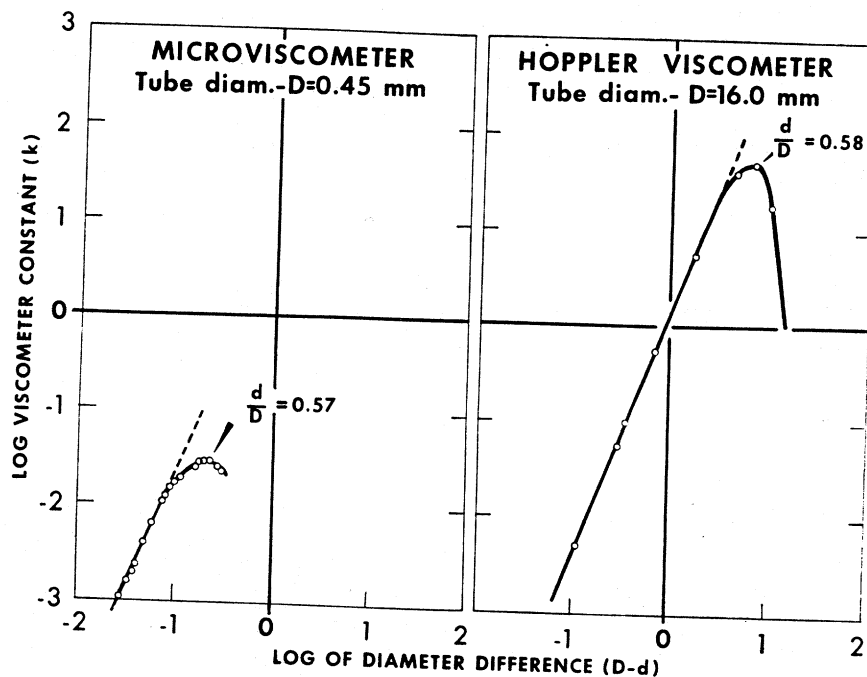


FIG. 1. The relationship between the instrument constant and the difference in diameter between the tube and ball.

ratio $\frac{d}{D}$. The ratio between the maximum values of k is equal to the square of the ratio between the tube diameters.

The relationships which have been noted are precisely those which would have been anticipated on the basis of dimensional analysis. Beyond the maximum in the region of small values of the bead diameter, k is proportional to the square of the bead diameter. This relationship is shown in Table 1, and begins to prevail when the bead diameter is about one-fourth the tube diameter. The rate of fall is then about one-sixth that which would have been observed had the fall been concentric and according to Stokes' Law.

The graphs are useful for estimating the time of transit, and they therefore serve as an aid in the selection of beads and tubes with respect to their diam-

TABLE 1

Relationship between viscometer constant and bead diameter for small diameters

Bead diameter (d) (mm.)	Tube const. (k) $\times 10^3$	$\frac{k}{d^2}$ experimental	$\frac{k}{d^2}$ calculated*
0.085	0.625	0.865	5.35
0.096	0.795	0.865	5.35
0.106	0.955	0.865	5.35
0.120	1.20	0.830	5.35
0.141	1.57	0.793	5.35

* Calculated according to Stokes' Law.

eters, in order to obtain transit times which fall within reasonable limits. For tubes 0.46 mm. in diameter, a minimum transit time is obtained of 3.7 sec. per centimeter per centipoise per unit density difference. This occurs when the bead diameter is about 0.26 cm. With smaller and larger beads, greater transit times are obtained. For constant $\frac{d}{D}$ the time will increase in proportion to the square of either d or D .

Type of motion executed by the bead. The force acting on the bead is proportional to the angle of inclination of the tube to the vertical. The product of the time and the cosine of the angle of inclination should, therefore, be constant. The results in Table 2 show, however, that the product increases as

TABLE 2
Variation of the time required for the bead to move 2.25 cm. with variations in the angle of inclination

Bead diameter (d)	Inclination (θ)	Time (t)	$t \cos \theta$
(mm.)	(degrees)	(sec.)	(sec.)
0.276	10.7	27.5	27.2
	29.6	34.0	29.5
	45.0	46.8	33.0
	60.4	79.5	39.2
	79.3	253.0	46.6

Tube diameter 0.490 mm.; temperature 30° C.; viscosity of glycerol solution, 5.47 centipoises.

the angle is increased. Observation under a microscope showed that the type of motion executed by the bead changed from a glide at an angle of approximately 10° to a progressively increasing roll as the angle was increased. The transition from a roll to a glide occurred at an angle which for any one tube was independent of the bead diameter and the viscosity of the fluid. The change in the type of motion would account qualitatively under ideal conditions for the observed relationship between velocity and the angle of inclination, as Weber (3) has shown in connection with the Höppler instrument.

A basis for rejection of viscometers. In Figure 2 the ratios between bead velocities at the two angles 29.6 and 10.7° are plotted as abscissae, and the frequency of their occurrence as ordinates. A skewed distribution is obtained. The most probable value of the ratio lies in the range 0.795-0.825. The arithmetic mean is 0.800 and the standard deviation is ± 0.03 . A hypothetical curve representing a normal frequency distribution has been superimposed on the bar drawing to emphasize the skewness. Abnormally low ratios between the velocities at the two angles are caused by bead imperfections and/or microscopic debris, and abnormally high values by distorted beads. Microviscometers functioning abnormally are largely eliminated and accuracy is enhanced if selection is based on the requirement that the ratio of velocities at the two stated angles should fall within the range of two standard deviations. The reproducibility of values obtained under these conditions is quite good (see Table 3). The estimated percentage deviation for a large number of measure-

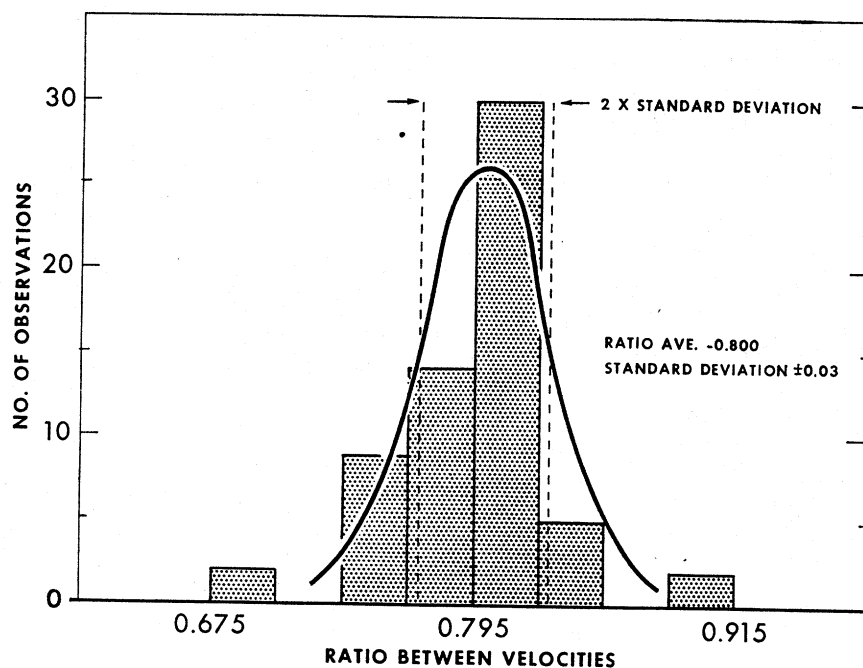


Fig. 2. Distribution curve for the occurrence frequency of the ratios between bead velocities at the two angles, 29.6 and 10.7°.

ments made on water and on glycerol solutions varying in viscosity from 0.8 centipoise to 35 centipoises was 0.3%. This estimate is based on the assumption that the percentage deviation is independent of the viscosity. The measured and literature viscosity values (5) agree quite closely. In one series of measurements for which the data are not shown, the ratio between the viscosities of a glycerol solution at 25 and 30° C. as determined with 15 different viscometers averaged 1.20 ± 0.01 centipoises, compared with the literature value (4) of 1.198.

The microviscometer has been developed chiefly for investigational work on evaporated milk. It should, however, find general application. Whenever extremely small volumes of material are available for measurements or proc-

TABLE 3
Comparison of viscosity values at 30° C. for glycerol solutions

Glycerol concentration	Viscosity microviscometer ^a	Literature values ^b	Difference
(%)	(centipoises)	(centipoises)	(%)
46.12	3.48	3.568	-2.5
54.47 ^c	5.35	5.352	0.0
64.89	9.99	9.956	+0.3
75.00	20.8	21.68	-4.0
80.00	33.5	34.92	-4.0

^a Bead diameter 0.270 mm., tube diameter = 0.416 mm., $\theta = 10.7^\circ$.

^b M. L. Sheely. Ind. and Eng. Chem., 24: 1060. 1932.

^c Solution used for standardization.

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essing, whenever flash sterilization or pasteurization is required, and whenever changes in viscosity on storage are to be followed with minimum disturbance of the sample, the microviscometer has much to recommend it, provided the ultimate in precision is not required in viscosity measurements.

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